The Transport and Deposition of Persistent Toxic Substances to the Great Lakes

I. The Capability of Specific Persistent Toxic Substances to be Subjected to Long Range Atmospheric Transport

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by

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Preface

This report was commissioned by the IJC International Air Quality Advisory Board. It is the first in a series of five closely related reports prepared for the Board which examine a set of persistent toxic substances identified in the Binational Virtual Elimination Strategy (BVES). The second report deals with the status and capabilities of available emissions inventories for BVES compounds. The third and fourth reports deal with modeling the atmospheric transport and deposition of BVES compounds to the Great Lakes and monitoring of these compounds in the Great Lakes region, respectively. The fifth report is a summary of the first four reports.

These reports were prepared as background documents for the IJC-sponsored Joint International Air Quality Board and Great Lakes Water Quality Board Workshop on Significant Sources, Pathways and Reduction/Elimination of Persistent Toxic Substances, held May 21-22, in Romulus Michigan.

The material presented here was collected and analyzed during the period from October 1996 through May 1997.

Acknowledgments

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Executive Summary

This report examines the potential for long range atmospheric transport and the status of emissions inventories of a group of persistent toxic substances identified by the Binational Virtual Elimination Strategy (BVES) for pollutants of concern in the Great Lakes Basin:

Alkylated lead	3,3'-Dichlorobenzidene
Mercury	4,4'-Methylene bis (2-Chloroaniline)
Cadmium	4-Bromophenyl Phenyl Ether
Tributyltin	Hexachloro-1,3-Butadiene
Aldrin	1,4-Dichlorobenzene
Dieldrin	Tetrachlorobenzenes
DDT	Pentachlorobenzene
DDD	Hexachlorobenzene
DDE	PCDD/F's
Mirex	PCB's
Toxaphene	Dinitropyrenes
Endrin	Benzo[a]Pyrene
Heptachlor	Phenanthrene
Heptachlor Epoxide	Anthracene
Hexachlorocyclohexanes	Benz[a]Anthracene
Methoxychlor	Perylene
Pentachlorophenol	Benzo[g,h,i]Perylene
Octachlorostyrene	PAH's (as a group)

The analysis is based on the characteristics of these compounds/groups that are likely to influence their potential for long-range air transport. The following analytical strategy was adopted.

First, it was determined whether the substances are in fact emitted into the atmosphere and actually detected in the atmosphere.

Second, an assessment was made, based on a consideration of the phase in which each compound is likely to occur in the atmosphere, of the degree to which each substance will respond to a group of factors that influence its fate in the atmosphere. These factors are:

- resistance to destructive chemical reactions in atmosphere;
- resistance to photolytic degradation;
- resistance to gas-phase rainfall washout;
- if and/or when the substance is associated with particles in the atmosphere, whether the substance is associated with *small* particles.

Third, the influences of these factors were used to estimate the substances' approximate lifetime in the atmosphere. Thus, for example, hexachlorobenzene is extremely resistant to all of the factors that tend to remove it from the atmosphere;

hence it has an atmospheric lifetime measured in years and moves over global distances. In contrast, a substance very susceptible to photolytic degradation while airborne may have a lifetime measured in minutes. The approximate overall lifetime is essentially based on the factor(s) which exerts the greatest influence on the removal of the substance from the atmosphere.

Fourth, evidence that the substances have been found at distances remote from their points of emission (for example, the occurrence of DDT in the Arctic) is considered, together with the estimated overall lifetime, to arrive at an overall Long-range Transport Rating.

Based on this procedure, it has been possible to classify the compounds/groups into four rough categories. Four overall LRT ratings are employed:

      Rating 1:   Atmospheric half-life, one year or more
                      Geographic distribution from sources: global

      Rating 2:   Atmospheric half-life, one week to a few months
                      Geographic distribution: 1,000-10,000 km (possibly global)

      Rating 3:   Atmospheric half-life, a few hours to a few days
                      Geographic distribution: 100-1,000 km

      Rating 4:   Atmospheric half-life, seconds to minutes
                      Geographic distribution: local

Table ES-1 lists the compounds/groups that fall into these categories. Four of them are in Rating 1 and are likely to be distributed globally. Three appear to be removed from the atmosphere so quickly as to fall into Rating 4 (although as noted, the evidence is not reliable). The remaining substances fall into the intermediate Ratings, 2 and 3, and are subject to transport over distances ranging from 100-10,000 km (with some possibly globally distributed), depending on their specific properties.

The grasshopper effect may be important for several of these compounds, and will probably serve to lengthen the effective scale of atmospheric transport; thus, for some of the compounds, the estimates of atmospheric lifetime and transport scale may represent lower bounds. Moreover, the rates of destruction in the atmosphere may be significantly slower in remote northern climates (due to lower concentrations of reactive species such as hydroxyl radical and lower temperatures), and so, the long range transport potential may again be underestimated for compounds traveling in these regions.

Table ES-1: Summary of Long-Range Air Transport Potential of Considered Compounds			
Rating			
1	2	3	4
Atmospheric Half Life			
1 year or more	1 week-few mos.	few hrs-few days	seconds-minutes
Geographic Distribution			
global	1,000-10,000 km (possibly global)	100-1,000 km	local
mercury	alkylated lead	aldrin(?)	aldrin (?)
hexachloro-1,3-butadiene	cadmium	heptachlor(?)	heptachlor (?)
tetrachlorobenzenes	DDT/DDD/DDE	4,4'-methylene bis (2-chloroaniline) (?)	4,4'-methylene bis (2-chloroaniline) (?)
pentachlorobenzene	mirex	tributyltin (?)	
hexachlorobenzene	toxaphene	heptachlor epoxide	
	hexachloro-cyclohexanes (HCH's)	methoxychlor	
	pentachlorophenol	dieldrin	
	octachlorostyrene	endrin	
	3,3'-dichloro-benzidene	4-bromophenyl phenyl ether	
	1,4-dichlorobenzene	phenanthrene	
	PCDD/F's	anthracene	
	PCBs		
	dinitropyrenes		
	benzo[a]pyrene		
	benz[a]anthracene		
	perylene		
	benzo[g,h,i]perylene		
	PAHs (as a group)		

The Capability of Specific Persistent Toxic Substances to be Subjected to Long Range Atmospheric Transport

A.   Introduction

Atmospheric deposition of pollutants is a major pathway for the entry of pollutants to the Great Lakes. Some of the pollution deposited from the air above the lakes originated from local sources, i.e., sources in the region immediately surrounding the lakes. However, some of the pollution that is deposited may have come from far away, transported in the atmosphere to the Great Lakes over long distances. For pollutants for which atmospheric deposition is an important contamination pathway, it is important to unravel the origin of the material that is deposited. If the bulk of it comes from local sources, then efforts to prevent deposition can be concentrated on reducing local emissions of the compound. On the other hand, if a significant portion of the pollutant comes from more distant sources, then efforts to lessen its impact must include a consideration of such long-range sources.

The Binational Virtual Elimination Strategy (BVES) identified a target list of 27 chemicals or chemical groups, including twelve Level I substances or groups and fifteen Level II substances or groups.

> Level I substances are the 11 Critical Pollutants identified by the IJC's Great Lakes Water Quality Board, plus one additional Critical Pollutant identified by the Lake Superior LaMP and the Lake Ontario Toxics Management Plan (Octachlorostyrene).[1]

> Level II Substances are those substances identified by the Canada-Ontario Agreement respecting the Great Lakes Basin Ecosystem (COA) as "Tier II" chemicals, plus additional substances of concern identified by LaMP and RAP processes and the Great Lakes Water Quality Guidance in the U.S.

> A list of the BVES compounds or groups is given in the following table.

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[1].   Note: Chlordane was also an additional Critical Pollutant identified on the BVES list, but it was inadvertently omitted from work scope for this analysis.

Table 1. Summary of Chemicals and Chemical Groups Considered in this Evaluation

Chemical or Group	Level	Notes
METALS / ORGANOMETALLICS		
Alkylated Lead	I	There are a range of compounds of environmental interest, including tetra-alkyl, tri-alkyl, and di-alkyl lead compounds, with methyl and ethyl alkyl groups alone and in combination.
Mercury	I	There are a range of inorganic and organic compounds containing mercury of environmental interest. These include elemental mercury, mercuric chloride, mercuric oxide, methyl mercury, dimethyl mercury, and possibly other compounds.
Cadmium	II	There are a range of inorganic cadmium compounds (including CdO, CdCl2, and others) and organic cadmium compounds of potential environmental interest.
Tributyltin	II	There are a range of tributyltin compounds of environmental interest.
ORGANOCHLORINE BIOCIDES		
Aldrin / Dieldrin	I	Dieldrin has been used as a biocide in its own right, and is also an environmental breakdown product of Aldrin
Chlordane	I	(inadvertently omitted and not included in this particular analysis)
DDT / DDD / DDE	I	DDD and DDE are breakdown products of DDT
Mirex	I	
Toxaphene	I	Toxaphene is a complex mixture of polychlorinated camphenes. There are over 30,000 theoretically possible congeners, with about 300 that may be likely to be present in the environment.
Endrin	II	
Heptachlor / Heptachlor Epoxide	II	Heptachlor Epoxide is an environmental breakdown product of Heptachlor
Hexachlorocyclohexane	II	There are five isomers: α-HCH, β-HCH, δ-HCH, ε-HCH and γ-HCH (lindane).
Methoxychlor	II	
Pentachlorophenol	II	
INDUSTRIAL / MISCELLANEOUS		
Octachlorostyrene	I	
3,3'-Dichlorobenzidene	II	
4,4'-Methylene bis (2-Chloroaniline)	II	
4-Bromophenyl Phenyl Ether	II	
Hexachloro-1,3-Butadiene	II	

Table 1. Summary of Chemicals and Chemical Groups Considered in this Evaluation

Chemical or Group	Level	Notes
CHLOROBENZENES		
1,4-dichlorobenzene	II	
Tetrachlorobenzene	II	There are three isomers: 1,2,3,4-tetrachlorobenzene and 1,2,3,5-tetrachlorobenzene are classified as Level II substances; 1,2,4,5-tetrachlorobenzene is not classified.
Pentachlorobenzene	II	
Hexachlorobenzene	I	
POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS (PCDD/F'S)		
2,3,7,8-TCDD	I	In addition to 2,3,7,8-TCDD/F, there are fifteen other penta-Cl through octa-Cl chlorinated dibenzo-p-dioxins and dibenzofurans that are 2,3,7,8-Cl-substituted that should be considered. In all, There are a total of 210 CDD/F's. In this analysis, all 17 toxic PCDD/F congeners were considered separately, although results are frequently presented for them as an entire group or as homologue groups (e.g, groups of PCDD/F with the same number of chlorine atoms)
2,3,7,8-TCDF	I	
POLYCHLORINATED BIPHENYLS (PCB'S)		
PCB's as a group	I	In all, there are a total of 209 possible PCB congeners. Many of these are commonly found in environmental samples. In this analysis, an attempt was made to consider the full set of PCB congeners, although results are frequently presented for them as an entire group or as homologue groups (e.g, groups of PCB's with the same number of chlorine atoms)
POLYCYCLIC AROMATIC HYDROCARBONS		
Benzo [a] Pyrene	I	
Dinitropyrenes	II	There are at least four isomers: 1,3-dinitropyrene; 1,6-dinitropyrene; 1,8-dinitropyrene; and 2,7-dinitropyrene. These may be emitted directly by sources, and, they may be formed by chemical reactions of pyrene with nitrogen species in the atmosphere.
PAH's as a group	II	There are many thousands of possible PAH compounds and derivatives. The target list specifies that the analysis of PAH's as group include (but not be limited to) the following specific PAH's: Phenanthrene Anthracene Benz[a]Anthracene Perylene Benzo[g,h,i]Perylene To create a group of PAH's for this analysis, the following PAH's were added, consisting of the universe of compounds considered in the EPA's 16-PAH list and the ATSDR 17-PAH list: Naphthalene / Acenaphthene Acenaphthylene / Fluorene Pyrene / Fluoranthene Chrysene / Benzo[b]Fluoranthene Benzo[j]Fluoranthene / Benzo[k]Fluoranthene Benzo[e]Pyrene / Dibenz[a,h]Anthracene Indeno[1,2,3-c,d]Pyrene

In order for a pollutant emitted to the atmosphere to be transported long distances in the atmosphere and be deposited in the Great Lakes, several conditions must be met:

- The pollutant must be emitted into the air;
- The atmospheric lifetime of the pollutant must be sufficient to allow it to be transported in the air over long distances;
- The pollutant must be capable of being deposited to the Lakes.

Emissions to the air will be considered in the second section of this report. This first section will consider the fate and transport of pollutants, if they were emitted to the air.

First, an attempt was made to assemble the physical/chemical properties for the substances of this study. For some of substances, there were no reported data for some or all of the relevant properties, and for some of the others, there were often conflicting data, where fairly widely diverse values for a given property were reported. It was beyond the scope of this study to attempt to evaluate the relative accuracy of different property values. Whenever possible, tabulations of "selected values" were used, in which the it is presumed that the authors selected the most likely value for a given property from among the available data.

Tables of physical and chemical properties assembled in Appendix A of this draft, and additional information is included as well, e.g., some of the methods used to estimate properties when no data were available.

B.   Atmospheric Loss Mechanisms and Atmospheric Lifetimes

B.1.   Introduction

1.   Vapor/Particle Partitioning. Compounds may exist in vapor or particulate phase; vapor particle partitioning will depend on the compound's physical-chemical characteristics, the detailed nature of the local airborne particulate, and the detailed local meteorological conditions — thus, V/P partitioning is not a static phenomenon; the V/P partitioning characteristics of a given compound will vary with location and time. The atmospheric fate of the compound will depend intimately on the vapor/particle partitioning characteristics.

2.   Chemical Reactions. Transformation reactions can occur in the gas phase, on particle surfaces, in liquid droplets or liquid shells around solid particles; different reactions may be important in different phases. Note: in some cases, the compound may be transformed to a more toxic species.

      A.   Direct photolysis reactions can occur, in which a compound absorbs ultraviolet light of a particular wavelength and is broken down.

      B.   Reactions with reactive species in the atmosphere can occur, such as reaction with hydroxyl radical, ozone, nitrate, hydrogen peroxide, chlorine, and others. For most species, reaction with hydroxyl radical is typically considered to be the most important chemical transformation reaction in the atmosphere.

3.   Deposition.

      A.   Dry deposition.   Both particles and vapors can be dry-deposited. By definition, dry deposition includes all atmospheric deposition of compounds to the earth's surface when there is no precipitation.

      B.   Wet deposition. Again, both particle-phase and vapor-phase material can be transported from the atmosphere to the ground through wet deposition processes.

B.2.   Vapor/Particle Partitioning

In order to understand and predict the fate and transport of atmospheric pollutants, their vapor/particle partitioning must be characterized (Bidleman, 1988).

As described in Appendix C, estimates were made using the adsorption-based theory of Junge (1977), with the subcooled liquid-phase vapor pressure substituted for the solid phase vapor pressure, as recommended by Bidleman (1988). The physical properties values used to make these estimates are given in Appendix A. A discussion of the theory and some of its limitations is presented in Appendix C-1. The calculation details are presented in Appendix C-2. The estimates are summarized in Appendix C-3, and comparisons are made to examples of vapor/particle partitioning measurements and/or estimates from the literature. In Appendix C-4, a detailed comparison of vapor/particle partitioning theoretical predictions and recent experimental measurements is presented.

In general, even though a relatively simple theoretical framework was used here to estimate the vapor/particle partitioning characteristics of BVES compounds in the atmosphere, the predictions appear to be reasonably consistent with the available experimental data.

An overall summary of the vapor/particle partitioning estimates is provided in Table 2, below. As mentioned above, details of the calculation procedure are provided in Appendix C.

Table 2. Overall Summary of Vapor/Particle Partitioning Estimates

Compounds which are predicted to exist almost entirely in the particle phase in the atmosphere (fraction adsorbed $\geq$ 98% under most conditions)	Compounds which are predicted to exist mostly in the particle phase in the atmosphere (fraction adsorbed $\geq$ 90% under most conditions)	Compounds which are predicted to exist in significant proportions in both the particle phase and the vapor phase as conditions vary	Compounds which are predicted to exist mostly in the vapor phase in the atmosphere (fraction adsorbed $\leq$ 10% under most conditions)	Compounds which are predicted to exist almost entirely in the vapor phase in the atmosphere (fraction adsorbed $\leq$ 2% under most conditions)
• Cadmium • OCDD/F • Dibenz(a,h)Anthracene	• HpCDD/F's • HxCDD/F's • Indeno(1,2,3-cd)Pyrene • Benzo(j)Fluoranthene (h) • Benzo(b)Fluoranthene (h) • Benzo(k)Fluoranthene (h) • Perylene (h) • Benzo(g,h,i)Perylene (h) • Benzo(a)Pyrene (h) • Benzo(e)Pyrene (h)	• Tributyltin oxide • DDT / DDD / DDE • Toxaphene • Methoxychlor • 3,3'-Dichlorobenzidene (b) • 2,3,7,8-TCDD/F • PeCDD/F's • PCB's (c) • Dinitropyrenes • Pyrene • Fluoranthene • Chrysene • Benz(a)Anthracene	• Mercury (e) • γ-HCH (Lindane) (a) • Octachlorostyrene • 4,4' Methylene bis- (b) (2-chloroaniline)	• Tetraethyl Lead (f) • Tetramethyl Lead (f) • Aldrin / Dieldrin • Mirex • Endrin • Heptachlor • Heptachlor Epoxide • α-HCH / β-HCH / δ-HCH • Pentachlorophenol (b) • Hexachloro-1,3-Butadiene • 4-Bromophenyl Phenyl Ether • Chlorobenzenes (d) • Naphthalene • Acenaphthene • Acenaphthylene • Fluorene (?) (g) • Phenanthrene (?) (g) • Anthracene

(a) γ-HCH (Lindane) is predicted to exist generally in the vapor phase but, under very cold conditions with high atmospheric particle surface area, as much as 3% of the atmospheric content may be associated with particles

(b) Compound is relatively water soluble (solubility may be pH dependent, e.g., Pentachlorophenol). Under high humidity conditions where the atmospheric aerosol might be expected to consist (in part) of liquid droplets, higher fractions of compound may be adsorbed into such liquid droplets.

(c) Different PCB congeners have different predicted behavior; monochloro-PCB's are predicted to be predominantly in the vapor phase under most conditions; dichloro- through decachloro-PCB's show increasing particle affinity, generally as the number of chlorines in the molecule increase.

(d) 1,4-Dichlorobenzene; Tetrachlorobenzenes; Pentachlorobenzene; Hexachlorobenzene

(e) The total fraction of atmospheric mercury associated with particles is uncertain, but is believed to be on the order a few, perhaps five, percent. Mercuric chloride is very soluble in water; if it is emitted then it could partition significantly to atmospheric water droplets.

(f) Atmospheric breakdown products of tetra-alkyl-lead compounds (e.g., trialkyl- and dialkyl- lead compounds) are very soluble in water; after they are formed, they may partition significantly to atmospheric water droplets.

(g) Evidence for less than full vapor/particle exchangeability exists; thus, compound may exist more on particles than predicted by theory which assumes full exchangeability.

(h) Simple adsorption theory suggests this compound may exist significantly in the vapor phase under some conditions, but, field measurements show that the compound exists primarily in the particulate phase in almost all measurements; therefore, the compound has been placed in this column.

B.3. Destruction and Transformation of Atmospheric Pollutants by Chemical Reactions and Photochemical Processes

Pollutants in the atmosphere can undergo a number of processes which lead to chemical transformation, i.e., processes in which in which the chemical identity of the compound is changed. The two potentially most important of these processes are generally considered to be chemical reaction (e.g., with hydroxyl radical or ozone) and direct photochemical transformation (e.g, as a result of absorption of uv light), although there can be other important processes for certain compounds in certain situations. Chemical reactions and photolytic processes can occur in both the vapor and particle phases in the atmosphere.

Reactions with hydroxyl radical — considered to be the most significant reaction for many atmospheric compounds — are generally considered to occur only in the vapor phase.[2] Other reactions, however, can occur in condensed phases. Reactions can occur, for example, in atmospheric water droplets. Many of the BVES compounds are relatively insoluble in water — with a few exceptions — and so atmospheric aqueous phase reactions, e.g., with hydrogen peroxide, will probably be relatively insignificant. Reactions can also occur in organic liquid-layer shells which may exist around atmospheric particles. For example, substituted phenols abundant in wood smoke particles react rapidly with PAH's (Odum *et al.* 1994); these reactions appear to be faster than those of PAH's with hexadecane in particles, representative of aliphatic hydrocarbons found in diesel exhaust (McDow *et al.*, 1994).

Like chemical reactions, photolysis can occur in the gas phase and in condensed phases. In addition to differences in photolytic rates of transformation between compounds based on chemical structures, substrate and solvent effects are frequently found in condensed phases.

Thus, for example, photodegradation rates of PAH's adsorbed to flyash are generally found to depend on the nature of the flyash, with rates on carbon-rich particles frequently lower than those on particles with less carbon [e.g., Baek et al. 1991 (review); Behymer and Hites, 1988 (example of a particular experiment)]. The protective effect may have to do with the light-absorbing nature of carbon-rich particles.

In a smog-chamber experiment, Pennise and Kamens (1996) found that PAH's and PCDD/F's were more stable on particles generated under <u>high-temperature</u> combustion of wood chips and PVC (and other chlorinated compounds) than on particles generated by <u>low-temperature</u> combustion of the same materials. On the high-temperature combustion, half-lives of particle-phase PAH's were on the order of 5-10 hours in an experiment in the summer (in North Carolina) and in the winter, some of the PAH's degraded with half-lives of between 6 -12 hours, with others showing no decay over a 6-hour daylight exposure. With the same high-temperature-combustion-

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[2]. Little or no information could be found regarding hydroxyl radical reactions in condensed phases, e.g., on the surface of particles. If this is an important phenomenon, then it is not well understood at the present.

generated particles, half-lives of particle-phase PCDD/F's were generally longer than those of the PAH's measured: particle-phase TCDD's half-life was estimated to be 6.8 hours in the summer and 68 hours in the winter, and OCDD's half-life was estimated to be 36 hours in the summer and 257 hours in the winter.[3]

As another example, particle-phase PCDD/F appears to be relatively invulnerable to photodegradation, based on measurements of PCDD/F adsorbed to flyash (Koester and Hites, 1992). This may serve to explain the observation that higher chlorinated PCDD/F congeners, which tend to be associated with the particle phase in the atmosphere, appear to be longer-lived in the atmosphere than lower chlorinated congeners, which exist significantly in the vapor phase. The difference in PCDD/PCDF congener profiles between atmospheric sources (where the distribution among congners is more uniform) and sinks (where the higher chlorinated congeners are disproportionately present) is consistent with this phenomenon.

Destruction/Transformation by Chemical Reaction

As mentioned above, the most important reaction for many gas phase atmospheric organic compounds is generally considered to be the reaction with hydroxyl radical (OH·) (e.g., Seinfeld, 1986; Finlayson-Pitts and Pitts, 1986). Reactions with other species — e.g. ozone, singlet oxygen, nitrogen oxides, chlorine — can be important under some conditions and with some compounds. In general, much less is known about the atmospheric reactions of these other reactive species in the atmosphere. Attention has been largely focused on hydroxyl radical attack because it is generally considered to be the most important.

Reaction rates with hydroxyl radical have been experimentally determined for a number of compounds, including a few of the compounds considered in this analysis. A summary of the data availability (for this project's compounds) for experimentally determined reaction rates with hydroxyl radical is summarized in Table 3. It can be seen that while data exist for some of the compounds considered, data for hydroxyl radical reaction rate are not available for most of the compounds considered in this analysis.

Because of the high cost of experimental measurements of the rate of hydroxyl radical reaction, it is common to attempt to estimate the reaction rate of a particular compound using structure-activity correlations. In such an approach, available data are analyzed for patterns which suggest how the rate is influenced by various aspects of the molecular structure. Atkinson and coworkers have made a number of the experimental measurements of hydroxyl radical rate constants (a list of many of their

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[3]. As is often the case, there were a number of factors in these experiments which complicate their extrapolation to the ambient atmosphere. Only particle-phase measurements were made, while some of the compounds may have existed to a certain extent in the vapor phase. As in any smog chamber experiment, wall losses can be significant. In addition, the particle concentrations in these experiments, 1000 - 7000 μg/m3 (10 - 100 times that found in the ambient atmosphere), and, the chlorine content of the particle-generating fuel was very high.

papers is given in Appendix D-5) and they have developed and refined a structure-activity model for organic compound reaction with hydroxyl radical.

Table 3. Summary of Experimentally Determined Hydroxyl Radical Rate Constants Available for Compounds Considered in this Evaluation		
category	specific species for which hydroxyl radical rate constant has been experimentally determined	notes
Mercury Compounds	• dimethyl mercury	
Alkyl-Lead Compounds	• tetraethyl lead • tetramethyl lead	
Chlorobenzenes	• 1,4-dichlorobenzene	
PCB's	• PCB 0: biphenyl • PCB 1: 2-monochloro-biphenyl • PCB 2: 3-monochloro-biphenyl • PCB 3: 4-monochloro-biphenyl • PCB 4: 2,2'-dichloro-biphenyl • PCB 7: 2,4-dichloro-biphenyl • PCB 11: 3,3'-dichloro-biphenyl • PCB 14: 3,5-dichloro-biphenyl • PCB 15: 4,4'-dichloro-biphenyl • PCB 28: 2,4,4'-trichloro-biphenyl • PCB 29: 2,4,5-trichloro-biphenyl • PCB 31: 2,4',5-trichloro-biphenyl • PCB 33: 2',3,4-trichloro-biphenyl • PCB 44: 2,2',3,5'-tetrachloro-biphenyl • PCB 47: 2,2',4,4'-tetrachloro-biphenyl • PCB 95: 2,2',3,5,6-pentachloro-biphenyl • PCB 110: 2,3,3',4',6-pentachloro-biphenyl • PCB 116: 2,3,4,5,6-pentachloro-biphenyl	• upper bound on reaction rate of biphenyl (PCB 0) with ozone is available
PAH's specifically identified on target list	• phenanthrene • anthracene	
PAH's added to list to create a "PAH group" for overall analysis	• naphthalene • acenaphthene • acenaphthylene • fluorene • pyrene • fluoranthene	• reaction rate of naphthalene with NO_3 has been determined • upper bound on reaction rate of naphthalene with ozone is available

The structure-activity model of Atkinson and coworkers has been presented in the following series of papers:

- Atkinson, R. (1987). "A Structure-Activity Relationship For the Estimation Of Rate Constants For the Gas-Phase Reactions Of OH Radicals With Organic-Compounds." International Journal Of Chemical Kinetics **19**(9): 799-828.

- Atkinson, R. (1988). "Estimation Of Gas-Phase Hydroxyl Radical Rate Constants For Organic Chemicals." Environmental Toxicology and Chemistry **7**(6): 435-442.

- Atkinson, R. and S. M. Aschmann (1992). "OH Radical Reaction-Rate Constants For Polycyclic Alkanes - Effects Of Ring Strain and Consequences For Estimation Methods." International Journal Of Chemical Kinetics **24**(11): 983-989.

- Kwok, E. S. C., R. Atkinson, et al. (1995). "Rate Constants For the Gas-Phase Reactions Of the OH Radical With Dichlorobiphenyls, 1-Chlorodibenzo-P-Dioxin, 1,2-Dimethoxybenzene, and Diphenyl Ether - Estimation Of OH Radical Reaction-Rate Constants For PCBs, PCDDs, and PCDFs." Environmental Science & Technology **29**(6): 1591-1598.

- Kwok, E. S. C. and R. Atkinson (1995). "Estimation Of Hydroxyl Radical Reaction-Rate Constants For Gas-Phase Organic-Compounds Using a Structure-Reactivity Relationship - an Update." Atmospheric Environment **29**(14): 1685-1695.

Meylan and Howard of the Syracuse Research Corporation (SRC: Syracuse, New York) have utilized the structure-activity relationships of Atkinson and colleagues — including the latest update (Kwok and Atkinson, 1995) — to create the Atmospheric Oxidation Rate Program.   A few changes to Atkinson's methodology were made which are believed to improve the accuracy of the estimates (Meylan and Howard, 1996). The latest version of this program was obtained from SRC (AOPWIN Version 1.82 (for Windows), 1996) and was used to make estimates for each of the compounds considered in this study.

A summary of the results of these estimates — including the estimated atmospheric half-life for reaction with hydroxyl radical — are presented in Appendix D-2 and D-3.

Appendix D-2 contains the a summary of the basic output from the program, including experimentally determined and estimated rate constants of the reaction with hydroxyl radical, experimental and estimated reaction rates and half-lives for reaction with ozone, and available data regarding reaction with NO_3.

Appendix D-3 contains estimates of an "adjusted" atmospheric half-life which factors in the effect of vapor/particle partitioning. To adjust the half-life, the values in Appendix D-2 were divided by the fraction of the compound predicted to exist in the vapor phase in the atmosphere. For example, for a compound which is predicted to exist 99% in the particle phase and 1% in the vapor phase, the vapor fraction equals 0.01, and, when the gas-phase half-life is divided by this fraction, it is increased by a factor of 100. In essence, the half-life is adjusted for the fact that the hydroxyl radical reaction is assumed to only proceed effectively in the vapor phase. Thus, compounds

that don't exist significantly in the vapor phase will not react quickly with hydroxyl radical, even if their "theoretically" predicted gas-phase reaction rate — based on structure activity relationships — would indicate a rapid reaction.

The screening level calculations performed here have been based on an average hydroxyl radical concentration of 1.5×10^6 molecules per cm^3, 12 hours of reaction per day, and reaction rates estimated generally at 25 $^\circ$C. These assumed screening level conditions may overestimate rate of destruction in northern climates, where temperatures may be substantially lower, and, in remote areas, where the hydroxyl radical concentrations may be lower. Thus, for pollutants being transported to the arctic — experiencing cooler temperatures and lower hydroxyl radical concentrations — the rate of chemical reaction may be substantially less than the screening level estimates given here. Thus, the extent of transport to the arctic may be increased.

Photolytic Destruction in the Atmosphere

As mentioned above, another pathway for the chemical transformation of compounds in the atmosphere is direct photolysis. In this phenomenon, a molecule absorbs a photon of ultraviolet (uv) radiation and is raised to a photochemically excited state. This state may be relatively unstable, and a chemical transformation process may occur. In such processes, the chemical nature of the molecule changes: bonds between one or more pairs of atoms in the molecule are broken or changed, and the new molecule may be slightly or radically different from the starting molecule.

Ultraviolet radiation with wavelengths below 290 nm is generally prevented from reaching the troposphere because it is absorbed in the upper levels of the atmosphere. Thus, for a compound to potentially undergo a photochemical transformation, it must be able to effectively absorb at electromagnetic radiation at at least some wavelengths greater than 290 nm.

Very few gas-phase measurements of photolysis have been attempted. Generally, measurements are made in the solution phase, i.e., the compound is dissolved in water or in some other solvent, or an adsorbed phase, i.e., on the surface of particles of a certain type.

Photolysis in the solution phase can be "direct" or "indirect". Indirect photolysis refers to the situation in which another species in the solution undergoes a photochemical transformation, and the product of this transformation subsequently reacts with the compound of interest. Sometimes the solvent itself participates in this process. In these cases, solution-phase photolysis rates can vary dramatically depending on which solvent is used. Thus, solution-phase photolysis rates cannot necessarily be applied to the atmosphere.

Photolysis measurements with compounds adsorbed to different substrates are also frequently made. For example, Freitag *et al.* (1985) report photodegradation rates for 100 compounds — including many of the BVES compounds — adsorbed to silica

gel. As mentioned above, experiments measuring the photodegradation of particle-associated materials have been made, for example, for PAH's (e.g., Behymer and Hites, 1988) and PCDD/F's (Koester and Hites, 1992). In the laboratory experiments of Koester and Hites (1992), essentially no photodegradation was observed for PCDD/F associated with flyash. This suggests that particle-associated PCDD/F in the atmosphere may be similarly resistant to photodegradation. However, as with the solution phase measurements above, it is difficult to directly extrapolate adsorbed-phase experimental results to ambient atmospheric conditions.

A very brief summary of available information about the possible importance of photolysis is given in the following table. Additional information about photolysis is presented in Appendix D-4.

Table 4. Summary of Information about Photolysis Rates (values in parentheses indicate a higher degree of uncertainty; values with question marks are even more uncertain)			
Chemical or Group	Level	Information About Photolysis Rates	photolytic resistance (0=vulnerable; 1=relatively invulnerable)
METALS / ORGANOMETALLICS			
Alkylated Lead	I		
Mercury	I	• Photolysis may be very important for organomercurials in the atmosphere (4) • However, elemental mercury will not be affected (5)	1
Cadmium	II		(1)
Tributyltin	II	• Slow photolysis observed in water; half-life estimated to be about 3 months (4)	1
ORGANOCHLORINE BIOCIDES			
Aldrin	I	• Aldrin does not absorb uv light at wavelengths greater than 260 nm in hexane; absorption maximum at 211 nm (6) • Vapor-phase photolysis reportedly significant in some tests, but reportedly not significant in others (4) • Photolysis can be important (11)	(½)
Dieldrin	I	• Dieldrin reportedly does not absorb uv light at wavelengths greater than 290 nm in hexane; absorption maximum at 218 nm (6) • However, photolysis can be important (11)	(½)
DDT	I	• Not expected to be significant based on lack of degradation in 7 days in one experiment and very slow rate of decay in another experiment (6)	1
DDD	I		(½)
DDE	I	• in water, photolysis half-life ranges from 1-6 days (4); • this same estimate applied to atmospheric DDE (6) • (reaction with OH probably more important)	½
Mirex	I	• direct photolysis half-life in sunlight in water determined experimentally to be on the order of 1 year (2); thus atmospheric photolysis should be relatively unimportant	1
Toxaphene	I	• Not expected to undergo direct photolysis (4)	1
Endrin	II	• Half-life estimated to be on the order of 5 - 9 days in intense summer sunlight; atmospheric information not available (4)	½
Heptachlor	II	• Half life measured in natural water to be 3.5 days (4) • Has absorption peaks above 290 nm (6) • Photolysis can form photo-heptachlor, a stable and toxic photo-product (11)	½
Heptachlor Epoxide	II	• Experimental evidence suggests that direct photolysis not very important, although indirect, i.e., sensitized, photolysis can be important in condensed phases	1

Table 4. Summary of Information about Photolysis Rates (values in parentheses indicate a higher degree of uncertainty; values with question marks are even more uncertain)			
Chemical or Group	Level	Information About Photolysis Rates	photolytic resistance (0=vulnerable; 1=relatively invulnerable)
α-Hexachlorocyclohexane	II		
β-Hexachlorocyclohexane	II	● less stable to uv than lindane, but not dramatically so (3)	¾ - 1
δ-Hexachlorocyclohexane	II		
γ-Hexachlorocyclohexane (Lindane)	II	● relatively stable to uv light (3) ● photolysis not expected to be important because chemical structure suggests very little absorption above 290 nm	1
Methoxychlor	II	● direct photolysis half-life in sunlight in water determined experimentally to be on the order of 1 month (2); thus atmospheric photolysis should be relatively unimportant	1
Pentachlorophenol	II	● fairly rapid photolysis when absorbed onto silica gel (3) ● photolysis important in aqueous solution (e.g., half-life on the order of hours) (4). ● photolysis estimated to be much more important than hydoxyl radical attack; half-life estimated to be on the order of <1 day (summer) to about 9 days (winter) at the latitude of Toronto, Canada (8).	¼
INDUSTRIAL / MISCELLANEOUS			
Octachlorostyrene	I		(1) ?
3,3'-Dichloro-benzidene	II	● Relatively unstable to uv light exposure when adsorbed to silica gel (similar to pentachlorophenol) (3) ● Found to be very unstable to photolysis in water (4) ● Exists in vapor and particle phase and so may be protected some of the time	¼ - ½
4,4'-Methylene bis (2-Chloroaniline)	II	● Absorption peak above 290 nm exists	?
4-Bromophenyl Phenyl Ether	II		?
Hexachloro-1,3-Butadiene	II		**?**
CHLOROBENZENES			
1,4-dichlorobenzene	II	● photolysis not expected to be significant (4) ● relatively stable against ultraviolet light (3)	1
Tetrachlorobenzenes	II	● (reasoning by analogy with other chlorobenzenes)	(1)
Pentachlorobenzene	II	● particularly stable against ultraviolet light (3)	1
Hexachlorobenzene	I	● photolysis not expected to be significant, based on experimental evidence (4) ● particularly stable against ultraviolet light (3)	1
POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS (PCDD/F'S)			

Table 4. Summary of Information about Photolysis Rates (values in parentheses indicate a higher degree of uncertainty; values with question marks are even more uncertain)			
Chemical or Group	Level	**Information About Photolysis Rates**	**photolytic resistance** (0=vulnerable; 1=relatively invulnerable)
PCDD/F's (as a group)	I	• Atkinson compared sunlight-water photolysis rates with estimated hydroxyl radical attack, and estimated that hydroxyl radical reaction would be faster, but not overwhelmingly so (7) • Photolysis in natural waters in sunlight estimated to be on the order of 1 - 7 days for 2,3,7,8-TCDD (data cited in 7) • All tetra- through octa CDD/F's exist to a certain extent (or almost completely) in the particle phase; thus, they will be somewhat protected against photolysis • In a smog-chamber experiment, it was found that PCDD/F's were more stable on particles generated under <u>high-temperature</u> combustion of wood chips and PVC (and other chlorinated compounds) than on particles generated by <u>low-temperature</u> combustion of the same materials. On the high-temperature combustion, half-lives of particle-phase, half-lives of particle-phase PCDD/F's were generally longer than those of the PAH's measured: particle-phase TCDD's half-life was estimated to be 6.8 hours in the summer and 68 hours in the winter, and OCDD's half-life was estimated to be 36 hours in the summer and 257 hours in the winter (10)	½
POLYCHLORINATED BIPHENYLS (PCB'S)			
PCB's (as a group)	I	• For PCB's with up to 6 chlorines, there does not appear to be any uv absorption (6) • For PCB's with 6 or more chlorines, there may be absorption bands above 290 nm (6); • However, portions of these heavier PCB's will be associated with particles; thus they *may* be somewhat protected, although particle-associated photolysis can occur.	¾ - 1

Table 4. Summary of Information about Photolysis Rates (values in parentheses indicate a higher degree of uncertainty; values with question marks are even more uncertain)			
Chemical or Group	Level	Information About Photolysis Rates	photolytic resistance (0=vulnerable; 1=relatively invulnerable)
POLYCYCLIC AROMATIC HYDROCARBONS			
Dinitropyrenes	II	• Photolytic degradation of particle-phase nitropyrenes occured with a half-life on the order of 0.5 to 2 hours in a smog chamber experiment, with degradation faster on wood smoke particles than on diesel exhaust particles (possibly because of the promotion of photodecay by methoxyphenols and methoxybenzaldehydes associated with wood smoke) (9)	¼
Benzo (a) Pyrene	I	• Direct photolysis half-life exposed to sunlight in water determined experimentally to be on the order of 1 hour (2); thus atmospheric photolysis may be relatively important • This compound had one of the shortest particle-phase photodegradation half-lives of nine PAH's investigated in a smog chamber experiment — 4 hours under summer conditions and 6 hours under winter conditions (10); however, the conditions were very different from ambient, and extrapolation of these results to the natural atmosphere is difficult.	½
Phenanthrene	II	• Direct photolysis half-life exposed to 313nm light in water determined experimentally to be on the order of 8.4 hours (2); thus atmospheric photolysis may be relatively important • This compound exists largely in the vapor phase	¼
Anthracene	II	• Has somewhat significant absorption peak at 360 nm (2) • Direct photolysis half-life in water determined experimentally to be on the order of 45 minutes for irradiation at 366 nm (2); thus atmospheric photolysis may be relatively important • This compound exists largely in the vapor phase	0 - ¼
Benz (a) Anthracene	II	• Direct photolysis half-life exposed to sunlight in water determined experimentally to be on the order of 3.3 hours (2); thus atmospheric photolysis may be relatively important • This compound had particle-associate photodegradation half-lives approximately twice as long as Benzo(a)Pyrene in smog chamber experiments (10).	½
Perylene	II		½
Benzo (g,h,i) Perylene	II	• This compound had some of the longest particle-phase photodegradation half-lives of nine PAH's investigated in a smog chamber experiment — 10 hours under summer conditions and essentially no decay under winter conditions (10); however, the conditions were very different from ambient, and extrapolation of these results to the natural atmosphere is difficult.	¾
Naphthalene	see note (1)	• Direct photolysis half-life exposed to 313 nm light in water determined experimentally to be on the order of 3 days (2); thus atmospheric photolysis may be somewhat important • This compound exists in the vapor phase	½

Table 4. Summary of Information about Photolysis Rates (values in parentheses indicate a higher degree of uncertainty; values with question marks are even more uncertain)			
Chemical or Group	Level	Information About Photolysis Rates	photolytic resistance (0=vulnerable; 1=relatively invulnerable)
Chrysene		• Direct photolysis half-life exposed to 313 nm light in water determined experimentally to be on the order of 4.4 hours (2); thus atmospheric photolysis may be relatively important • This compound (measured together with Benz(a)Anthracene) had mid-range particle-phase photodegradation half-lives in a study of nine PAH's in a series of smog chamber experiments — 6 hours under summer conditions and 12 hours under winter conditions (10); however, the conditions were very different from ambient, and extrapolation of these results to the natural atmosphere is difficult.	¾
Pyrene		• Has a significant absorption peak at 295 nm (2) • Direct photolysis half-life exposed to 313 and 366 nm light in water determined experimentally to be on the order of 0.68 hours (2); thus atmospheric photolysis may be relatively important • This compound had mid-range particle-phase photodegradation half-lives in a study of nine PAH's in a series of smog chamber experiments — 6 hours under summer conditions and 8 hours under winter conditions (10); however, the conditions were very different from ambient, and extrapolation of these results to the natural atmosphere is difficult.	½
Dibenz(a,h)anthacene		• Found to have one of the most rapid photodegradation rates of all PAH's tested in an experiment with compounds adsorbed to silica gel (3) • This compound had mid-to-long particle-phase photodegradation half-lives in a study of nine PAH's in a series of smog chamber experiments — 6 hours under summer conditions and 8 hours under winter conditions (10); however, the conditions were very different from ambient, and extrapolation of these results to the natural atmosphere is difficult.	½
PAH's (as a group)	II		

Table 4. Summary of Information about Photolysis Rates (values in parentheses indicate a higher degree of uncertainty; values with question marks are even more uncertain)			
Chemical or Group	Level	Information About Photolysis Rates	photolytic resistance (0=vulnerable; 1=relatively invulnerable)

References and Notes for above Table

(1) Individual compounds added to consider PAH's as a group include: Naphthalene: Acenaphthene; Acenaphthylene; Fluorene; Indeno(1,2,3-c,d)Pyrene; Dibenz (a,h) Anthracene; Benzo(b)Fluoranthene; Benzo (j) Fluoranthene; Benzo(k)Fluoranthene; Benzo(e)Pyrene; Pyrene; Fluoranthene; and Chrysene

(2) Harris, J., 1982: "Aqueous Photolysis," in Handbook of Chemical Property Estimation Methods, edited by Lyman, W., et al. Washington D.C.: American Chemical Society. pp 8-1 to 8-43.

(3) Freitag et al., 1985: "Environmental Hazard Profile of Organic Chemicals," Chemosphere 14(10): 1589-1616.

(4) Information summarized from Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profile for the substance (documents released over several different years; most in 1993-1995)

(5) Schroeder et al., 1991: "Transformation Processes Involving Mercury Species in the Atmosphere — Results from a Literature Survey," Water, Air and Soil Pollution 56: 653-666.

(6) Howard, P.J., et al., 1991: Handbook of Environmental Degradation Rates, Boca Raton FL: CRC Lewis Press

(7) Atkinson, R.,1991: "Atmospheric Lifetimes of Dibenzo-p-dioxins and Dibenzofurans," Science of the Total Environment 104: 17-33.

(8) Bunce, N.J., et al., 1991: "A Model for Estimating the Rate of Chemical Transformation of a VOC in the Troposphere by two Pathways: Photolysis by Sunlight and Hydroxyl Radical Attack," Chemosphere 22(3-4):305-315.

(9) Fan, Z, R.M. Kamens, et al. (1996). "Photostability of Nitro-Polycyclic Aromatic Hydrocarbons on Combustion Soot Particles in Sunlight." Environmental Science and Technology 30(4): 1358-1364.

(10) Pennise, D. M. and R. M. Kamens (1996). "Atmospheric Behavior Of Polychlorinated Dibenzo-P-Dioxins and Dibenzofurans and the Effect Of Combustion Temperature." Environmental Science & Technology 30(9): 2832-2842. [Note: the high temperature combustion results of this paper were used in providing input to the above table.]

(11) Bidleman (1997) (personal communication)

B.4. Removal of Vapor-Phase Pollutants from the Atmosphere by Wet and Dry Deposition

Vapor-phase pollutants can be removed from the atmosphere by wet or dry deposition.

Wet Deposition of Vapor Phase Material

Unless the compound is relatively water soluble, the removal of vapor-phase material by wet deposition will generally be relatively insignificant, although there may be some exceptions (see below). A qualitative analysis of the "gas-phase washout" phenomenon is presented in Appendix D-1. Estimates were made of the relative importance of this phenomenon for each of the compounds considered in this analysis, based on each compound's estimated Henry's Law constant (a measure of the partitioning between the air and water phases) and the extent to which the compound is expected to exist in the gas phase.

For most of the considered compounds, gas-phase washout is expected to be an insignificant atmospheric removal process (the details are given in Appendix D-1). For one of the compounds -- 4,4'-methylene bis(2-chloroaniline, "MBOCA") — the qualitative analysis suggests that suggests very rapid removal from the atmosphere by rainfall. The analysis also indicated that mercuric chloride ($HgCl_2$), 3,3'-Dichlorobenzidene, pentachlorophenol, and at least some of the hexachlorocyclohexane isomers might be removed relatively rapidly from the atmosphere by rainfall. Interestingly, mercury in precipitation has been found to be correlated with concentrations of chloride ion, suggesting that an important form of mercury in precipitation is $HgCl_2$ (Keeler, Glinsorn, and Pirrono, 1995).

It is likely that the situation regarding gas-phase washout may be more complicated than the simplified screening analysis used here.

For example, this analysis suggested that alpha-HCH and gamma-HCH — predicted by the simplified vapor/particle partitioning theory used here to exist largely in the vapor phase — would not be appreciably washed out by precipitation. However, they are found in significant concentrations in precipitation (e.g., Chan *et al.*, 1994; Hoff *et al.*, 1996). With these compounds, it is not clear if the vapor/particle characterization of this analysis is in error, or, if other factors are contributing to the larger-than-anticipated washout.

Similarly, Ligocki *et al.* (1985ab) found significant apparent gas-phase washout for many somewhat volatile PAH's in experimental measurements, in some cases greater than the measured particle-phase washout efficiencies for the same

compounds. While interpretation of these measurements is somewhat difficult[4], they suggest an apparently higher degree of precipitation washout of these compounds than anticipated in this screening analysis.

Finally, chemical reactions may influence the degree to which a pollutant is absorbed into precipitation. For example, elemental mercury — which is believed to be relatively insoluble in water — may be slowly absorbed but then subsequently oxidized (by dissolved ozone or other oxidants) to the more soluble divalent Hg^{+2} in aqueous droplets. This process may result in a relatively significant amount of mercury being incorporated into atmospheric water droplets (which may fall to the earth's surface as precipitation). Alkylated lead compounds may also be affected in this way. Tetraethyl lead and tetramethyl lead are relativlely insoluble, but their atmospheric breakdown products (e.g., triethyl lead^{+1}, trimethyl lead^{+1}) may be highly soluble.

Dry Deposition of Vapor Phase Material

Dry deposition of vapor-phase material can be a relatively significant removal mechanism of pollutants from the atmosphere. At the surface of the earth, substantial quantities of atmospheric pollutants can be adsorbed into soil, vegetation (e.g., Calamari et al., 1991), and surface water. There are many interesting consequences of this phenomenon.

First, gas exchange of some pollutants with lakes can be important to the overall mass balance of the pollutant in the lake. Gas exchange of semivolatile pollutants with the Great Lakes may be a very significant phenomenon, although data to assess its relative importance are scarce (e.g. Hoff et al., 1996). Even if a pollutant is relatively insoluble in water, partitioning to suspended sediment and other organic matter in the water column can allow the transfer of vapor-phase atmospheric pollutants to be thermodynamically possible under certain conditions. There have been several studies that have attempted to estimate the direction and rate of gas exchange of different pollutants with one or more of the Great Lakes. Examples are given in the following table.

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[4]. In these measurements, vapor and particle phase concentrations were measured near the ground, and compared with operationally dissolved and particulate concentrations of the same pollutant in precipitation samples. Since the ground-level concentration of pollutant in the vapor and particle phases is not necessarily the same as that at higher elevations, the significance of washout ratios estimated from such measurements is an issue.

Table 5. Examples and Reviews of Analyses of Gas Exchange with Lakes	
Hoff *et al.* (1996)	a range of compounds measured in the Great Lakes region
Bidleman and McConnell (1995)	review of measurements and analyses
Hoff, Bidleman, & Eisenreich (1993)	toxaphene
Achman, Hornbuckle, & Eisenreich (1993) Jeremiason, Hornbuckle, & Eisenreich (1994) Hornbuckle *et al.* (1995) Honrath, Sweet, & Plouff (1997)	PCB's
Baker & Eisenreich (1990)	PAH's and PCB's
McConnell, Cotham, & Bidleman (1993) Ridal *et al.* (1996)	α-HCH and γ-HCH

Second, the gas-phase adsorption of pollutants into vegetation can be an extremely significant pathway of the pollutant into terrestrial food chains. A significant proportion of the overall exposure of the general population to PCDD/F, for example, is thought to arise largely from consumption of contaminated meat and milk products. The contamination in the meat and milk is believed to be present because of adsorption of vapor-phase PCDD/F into vegetation which is later consumed, for example, by dairy cows and beef cattle.

Third, material adsorbed to soil at the earth's surface may be resuspended as dust particles and contribute to — at least — the ground level atmospheric concentrations of pollution and the apparent ground level deposition of pollution. This phenomenon may at least partly serve to explain the recent findings that dry deposition of PCB's is apparently dominated by very large particles (e.g. Holsen et al., 1991; Lee et al., 1996). A theoretical analysis of this phenomenon in relation to dioxins and furans was recently presented by Kao and Venkataraman (1995). They concluded that while the re-entrainment of dioxin-laden dust particles would probably not contribute more than about 4% of ambient, ground level atmospheric dioxin concentrations, the particles could account for as much as 70 - 90% of the apparent dry deposition in urban areas and as much as 20 - 40% of the apparent dry deposition in rural areas (where the soil concentrations of PCDD/F are lower).

Finally, it has recently been hypothesized that certain compounds might be adsorbed at the earth's surface at a particular location and then re-emitted to the atmosphere at a later time (e.g., when the temperature has increased). This so-called "grasshopper effect" is thought to contribute to a global fractionation of semivolatile compounds, in which some compounds may be (over time) preferentially partitioned to colder climates. The strong, apparent correlation of certain compounds in the atmosphere with ambient temperature (e.g., Hoff et al., 1992a,b) provides evidence that this phenomenon can be important. Discussions and reviews of this phenomenon are given in a series of articles by Wania and Mackay (1993ab, 1995, 1996).

This grasshopper effect is an area of current research, and it is difficult to make quantitative estimates at this time. In the following, a brief discussion will be given, and is considered to be only a preliminary consideration of this phenomenon.

The tendency of a given compound to be subject to this phenomenon will depend, of course, on the detailed nature of the various physical and chemical interactions between the pollutant and different surfaces to which it initially deposits, and on a variety of additional factors (e.g., meteorological conditions, the ability of the compound to survive in the atmosphere during each hop, etc.) The grasshopper effect is believed to be most important for persistent compounds of intermediate volatility. Compounds that are very volatile will not deposit readily, and compounds with very low volatility will be less likely to be revolatilized once they are deposited. It appears that the grasshopper effect may be important for many of the BVES compounds, particularly for many of the compounds in the right-most three columns of Table 2, i.e., the compounds which exist with significant — or predominant — proportions in the vapor phase in the atmosphere.

As discussed by Bidleman et al (1997), some compounds might be considered to be subjected to only a single "hop", in which they are emitted and then deposited, and then are not revolatilized significantly. These compounds would be said not to exhibit the grasshopper phenomenon. Other compounds — which do exhibit the phenomenon — might be considered to be able to undergo multiple hops.

Wania and McKay (1996) have classified compounds into 4 qualitative classes, based on their tendency to be subjected to the grasshopper effect. A first class of compounds are least likely to be subject to the phenomenon, and these include compounds such as PCB's with eight or more chlorines, PCDD/F's with 4 to 8 chlorines, PAH's with 4 or more rings, and mirex. These compounds and those similar to them are believed to only undergo one hop — i.e., once they are deposited, they are not significantly re-emitted. A second class of compounds is capable of several hops, especially in somewhat warm climates, but, ultimately may tend to preferentially deposit in mid-latitude regions. Compounds in this class include PCB's with four to eight chlorines, PCDD/F's with 2 to 4 chlorines, PAH's with 4 rings, toxaphene, DDT's, and chlordanes.[5] A third class of compounds — including penta- and hexachlorobenzene, mono- through tetra-chloro PCB's, 3-ring PAH's, HCH's, and dieldrin — may undergo many hops and ultimately be preferentially deposited in polar regions. A last class of compounds — including chlorobenzenes with 1 to 4 chlorines, monochloro-PCB's, and two-ring PAH's (e.g., naphthalene) — are so volatile that they may not be deposited significantly from the atmosphere. These classes would seem to be a very useful start towards classifying the various BVES compounds with respect to the grasshopper

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[5]. As can be seen, the categories appear to overlap somewhat, with certain classes of compounds. For example, PCDD/F's with 4-8 chlorines are in the first category, and PCDD/F's with 2-4 chlorines are in the second category; thus, it would appear that PCDD/F's with 4 chlorines are in both categories. In fact, different compounds within a given homologue group can exhibit different properties — in this case, for example, different tetrachlorodibenzo-p-dioxin congeners will have different physical-chemical properties, and so, it is possible that group spans two different classes.

phenomenon.

One question that arises is the length of time and distance traveled between hops, or in the case of a single hop-compound, the atmospheric lifetime characteristic of a single hop.

In an attempt to model the long-range transport of PCDD/F's in the U.S. and southern portions of Canada, the dry deposition of vapor phase material was found to be approximately as significant a removal pathway as particle-phase deposition (wet + dry) for 2,3,7,8-TCDD, a compound which exists about equally in the vapor and particle phases in the atmosphere (Cohen et al., 1995). In this example, the atmospheric lifetime of 2,3,7,8-TCDD relative to vapor phase dry deposition can be estimated (very approximately) to have been on the order of one week based on its comparability to particle phase (wet + dry) deposition.[6] That is, the time-scale for a single hop for vapor-phase 2,3,7,8-TCDD appears to have been on the order of one week (for the calculations done in this study).

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[6]. As discussed below, a rough estimate of the atmospheric lifetime for particle phase deposition processes (wet + dry) is on the order of 7 - 10 days.

B.5. Removal of Particle-Phase Pollutants from the Atmosphere by Wet and Dry Deposition

Particles in the atmosphere are generally classified into three separate size ranges: the "nucleation range", comprising particles with diameters less than approximately 0.05 μm (1 μm = 1×10^{-6} meters); the "accumulation range", comprising particles with diameters roughly between 0.05 μm and about 2 μm; and the "coarse particle range", consisting of particles with diameters greater than about 2 μm in diameter (e.g., Lodge, 1981; Prospero et al., 1983; Seinfeld, 1986; Pacyna, 1995). Particles in the two smallest ranges are sometimes grouped together in a "fine particle" category.

Particles in the nucleation range are subject to coagulation and incorporation into larger particles; thus, the material contained in them is generally transferred to larger particles, generally in the accumulation range. The time scale for such processes is on the order of hours (Pacyna, 1995). Particles greater than about 10 μm -- generated primarily by mechanical actions and wind erosion -- have relatively fast sedimentation rates, and can be removed relatively quickly by dry deposition from the atmosphere. Typical residence times for such large particles are on the order of a few hours. Particles in the accumulation range, on the order of 1 μm in size, do not efficiently coagulate into larger particles, and do not have large sedimentation velocities. They can be removed by wet and dry deposition processes, but, have atmospheric lifetimes on the order of 7 - 10 days (Pacyna, 1995; Prospero, 1983). Since the fate of nucleation range particles is often to end up quickly incorporated into the accumulation range, the atmospheric lifetime of the *pollutants* associated with these small particles is also on the order of 7-10 days.

Windblown soil particles are often relatively large, and fall into the coarse particle range. However, a fraction of such aerosols are fine particles (e.g., Pacyna, 1995).

Manchester-Neesvig and Andren (1989) used an average residence time for atmospheric particles in the Northern Hemisphere of 6 days in their estimation of the particle-mediated atmospheric lifetime of particle-bound PCB's.

Particles emitted from combustion and incineration processes will generally fall into the fine-particle category. Vapor/particle partitioning is often considered a surface phenomenon, and partitioning to particles is often assumed to scale with particle surface area.[7] That is, when vapor-phase material condenses onto particles, it is considered to do so relatively equally onto each available surface, on a per-area basis. The most significant portion of the surface area available for adsorption is with the fine particles. Thus, for exchangeable, semivolatile compounds that partition between the particle and vapor phases, a significant fraction of their particle-associated mass will lie in the fine-particle range.

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[7]. Compounds can also be *absorbed into* semi-liquid organic surface layers around atmospheric particles, and thus vapor/particle partitioning is not strictly a surface phenomenon.

Measurements of the size of particles to which semivolatile compounds in the atmosphere are absorbed are difficult, and many factors can bias the results (e.g., Poster et al., 1995). Examples of attempted measurements of the average particle size in which specific pollutants are found in the atmosphere are summarized in Table 6.

In summary, to the extent that they are associated with particles, the pollutants of this analysis are estimated — on the basis of theoretical and experimental considerations — to exist predominantly in the fine particle range, with sizes less than approximately 2 μm. The atmospheric lifetime of pollution associated with such particles will be highly variable depending on meteorological conditions, source characteristics, and particle characteristics, but, perhaps the average atmospheric lifetime of such particle-associated pollution will be on the order of 1 week. Depending on the meteorological conditions, such particles could travel hundreds to thousands of kilometers in the atmosphere before they are removed by wet or dry deposition processes.

	Table 6. Examples of Measured Average Atmospheric Particle Sizes of Selected Pollutants	
	Note: for pollutants which exist both in the vapor and particle phase, the measurements generally refer to the particle phase only	
Pollutant	**Atmospheric Particle Size Information**	**References Notes**
Metals and Metallic Compounds		
Cadmium	• The mass-weighted average particle size in the atmosphere was estimated to be approximately **0.84 μm**, based on a number of ambient measurement studies.	(1)
Organic Biocides		
DDT / DDE	• At ambient temperatures between 267 and 275 °K, 73-88% of atmospheric DDT and 18-41% of atmospheric DDE was found in the particle phase in measurements at the University of Bayreuth, Germany (Kaupp and Umlauf, 1990). The concentration of DDT and DDE in the atmosphere ranged from 24-74 and 6.2-11 pg/m3, respectively. **Particulate-associated DDT and DDE was largely found on particles less than 1 μm in diameter.**	(3)
Polychlorinated Dibenzo-*p*-Dioxins and Dibenzofurans (PCDD/F's)		
PCDD/F's	• Three samples collected in a rural area • PCDD/F found in both vapor-phase and particle-phase • Approximately 90% of particle-phase PCDD/F's found on particles less than 1.35 μm in diameter; • Approximately 50 - 60% of the particle-phase PCDD/F's found on particles less than 0.45 μm in diameter; • Smaller particles tended to have higher concentrations of PCDD/F's than bigger particles, consistent with a surface-area-related partitioning phenomena.	(4)
Polychlorinated Biphenyls (PCB's)		
PCB's	• five samples collected; • average results given in paper for dichloro-, trichloro-, tetrachloro-, pentachloro-, hexachloro-, heptachloro-, and octachloro-PCB's, and for total PCB's; • there were differences among the different homologue groups, but, the results can be summarized as follows: • approx. 38 - 52% of particle-phase PCB's found on particles < 1 μm diameter; • approx. 46 - 67% of particle-phase PCB's found on particles < 2.5 μm diameter; • approx. 80 - 93% of particle-phase PCB's found on particles < 10 μm diameter; • approx. 98 - 99.9% of particle-phase PCB's found on particles < 25 μm diameter; • The particle size distribution of particle-associated PCB's in the atmosphere appeared to be bimodal, with a peak in the fine mode at particle diameters	(5)

Table 6. Examples of Measured Average Atmospheric Particle Sizes of Selected Pollutants

Note: for pollutants which exist both in the vapor and particle phase, the measurements generally refer to the particle phase only

Pollutant	Atmospheric Particle Size Information	References Notes
Polycyclic Aromatic Hydrocarbons (PAH's)		
Fluoranthene	• 95% of particle-phase material found on particles ≤ 1.7 μm • 55% of particle-phase material found on particles ≤ 0.49 μm	(2)
Pyrene	• 96% of particle-phase material found on particles ≤ 1.7 μm • 61% of particle-phase material found on particles ≤ 0.49 μm	(2)
Benz(a)Anthracene	• 97% of particle-phase material found on particles ≤ 1.7 μm • 58% of particle-phase material found on particles ≤ 0.49 μm	(2)
Chrysene	• 96% of particle-phase material found on particles ≤ 1.7 μm • 57% of particle-phase material found on particles ≤ 0.49 μm	(2)
Benzo(b) Fluoranthene	• 96% of particle-phase material found on particles ≤ 1.7 μm • 50% of particle-phase material found on particles ≤ 0.49 μm	(2)
Benzo(k) Fluoranthene	• 97% of particle-phase material found on particles ≤ 1.7 μm • 56% of particle-phase material found on particles ≤ 0.49 μm	(2)
Benzo(e)pyrene	• 96% of particle-phase material found on particles ≤ 1.7 μm • 55% of particle-phase material found on particles ≤ 0.49 μm	(2)
Benzo(a)pyrene	• 95% of particle-phase material found on particles ≤ 1.7 μm • 23% of particle-phase material found on particles ≤ 0.49 μm	(2)
Indeno(1,2,3-cd) pyrene	• 98% of particle-phase material found on particles ≤ 1.7 μm • 61% of particle-phase material found on particles ≤ 0.49 μm	(2)
Benzo(g,h,i) perylene	• 97% of particle-phase material found on particles ≤ 1.7 μm • 59% of particle-phase material found on particles ≤ 0.49 μm	(2)

References:

(1) Milford and Davidson (1985)

(2) Poster, Hoff, and Baker (1995) ... Ambient size-segregated sample at Egbert, Ontario, February 8, 1993; rural location. Similar results found in an urban-area sample in Chicago, Illinois, in the same study.

(3) Kaupp and Umlauf (1990) ... At ambient temperatures between 267 and 275 °K, 73-88% of atmospheric DDT and 18-41% of atmospheric DDE was found in the particle phase in measurements at the University of Bayreuth, Germany (considered to be a rural location by the authors). The concentration of DDT and DDE in the atmosphere ranged from 24-74 and 6.2-11 pg/m3, respectively.

(4) Kaupp, Towara, and McLachlan (1994) ... Three samples with mean ambient temperatures from 17.4 - 21.9 °C. Samples taken at the University of Bayreuth, Germany (a rural location).

(5) Lee et al., 1996 ... Tainan City, Taiwan

C. Empirical Evidence of Long Range Transport

There are many uncertainties in our understanding of the fate and transport of pollutants in the atmosphere. Even for compounds that have been the subject of numerous investigations (e.g., PCB's), there are numerous uncertainties that make an extremely accurate estimate of their atmospheric behavior difficult. For many of the compounds considered in this analysis, the lack of data on physical-chemical properties and/or the lack of extensive measurement in the atmosphere make such estimates even more difficult.

Given this situation, another approach to evaluating the long range atmospheric transport of a given compound is to consider various types of empirical evidence.

Perhaps the most straightforward measure of a substance's potential to be transported long distances in the atmosphere is the extent to which it is found in remote locations, far removed from any sources. If the pollutant is found at such remote sites at significant levels in the atmosphere, in atmospheric deposition (e.g., precipitation), or in vegetation, then it can be generally concluded that the pollutant in question reached these sites as a result of long-range atmospheric transport. Measured concentrations in fish, terrestrial animals and humans can be more difficult to interpret, as other (non-atmospheric) exposure pathways may be important (e.g., ocean circulation). Recent reviews of this phenomenon include those by Barrie et al. (1992), Wania and Mackay (1996), and Kurtz (1990).

Another, perhaps less straightforward, type of empirical evidence is the relative concentrations of a given compound in places which are very distant from one another. If the concentration in the air, in precipitation, or in vegetation is very similar in several widely separated locations, or, follows consistent patterns (e.g., a latitudinal pattern in which temperature effects appear to play a significant role), then this is evidence that there is a widespread distribution of the compound in the atmosphere. Thus, for example, the fact that the level of hexachlorobenzene in the air is relatively constant — at concentrations on the order of 100 pg/m^3 — from location to location in ambient air measurements around the world (e.g., Wania and Mackay, 1993; Risebrough, 1990; Gatz et al., 1994; Oehme, 1991) suggest that the distribution of HCB is essentially global.

The fact that similar concentrations might be found in diverse locations does not necessarily mean that long range air transport is occurring, however. Such a finding might simply be an indication that the source strengths are similar in each area. Such a situation might be the case, for example, for pentachlorophenol (PCP). It is widely used as a wood preservative, and can volatilize to the air from treated wood. PCP was recently measured in pine needles[8] at seventeen different locations in Saskatchewan,

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[8]. The dominant pathway by which PCP enters pine needles is through the air. Thus, measurements of the concentrations of PCP in pine needles gives information about the levels in the atmosphere.

Canada (Thompson and Treble, 1995). Fifteen of the samples were taken in various locations in the city of Regina, and two samples were taken sites relatively far away (Saskatoon, a city 250 km northwest of Regina, and Yellowgrass, a rural community 80 km southeast of Regina). Similar concentrations of PCP were found in pine needles at all locations. The similarity of the samples *could* be indicative of widespread PCP distribution resulting from long-range atmospheric transport. However, the similarity could also simply be the result of widespread emissions of PCP resulting from its ubiquitous use a wood preservative.

By the same token, when there *are* large spatial variations in environmental concentrations, this does not prove that long range atmospheric transport is *not* occurring. One can imagine a case where relatively strong local sources create moderate or even intense local concentration gradients, and these local contributions are superimposed onto a regional, continental, or global "background" resulting from widespread atmospheric dispersal.   This may well be the case, for example, for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F's). There are many sources of these compounds, including many strong point sources. Certainly, in the vicinity of a strong source, the environmental concentrations may be found to be relatively high. However, if the source did not exist, the concentrations would not be "zero" — long range transport from other locations will almost certainly contribute to environmental levels at the given site.

In sum, the interpretation of the degree of spatial variability as providing evidence for or against long-range atmospheric transport of a given pollutant depends on spatial variability of the pollutant's sources.

Examples of empirical evidence supporting (or not supporting) long range atmospheric transport for compounds considered in this analysis are given in Table 7. For some of the compounds, empirical evidence was not found.

Table 7. Examples of Empirical Evidence for Long Range Atmospheric Transport		
Chemical or Group	**Level (b)**	**Examples of studies which have found compound in remote areas, i.e., areas believed to be distant from any source of the particular compound**
METALS / ORGANOMETALLICS		
Alkylated Lead	I	• Lobinski et al. (1994a) found diethyl, triethyl, dimethyl, and trimethyl lead compounds in fresh Greenland snow. Tetraethyl and tetramethyl lead were at or below detection limits. The authors suggest that the atmospheric lifetime of diethyl and triethyl lead compounds may be longer than predicted based on laboratory experiments. Organolead is enriched over inorganic lead in long range atmospheric transport, suggesting that organolead compounds are longer-lived in the atmosphere than inorganic lead compounds. • Lobinski et al. (1994b) found diethyl and triethyl lead compounds in Greenland snow cores; these are atmospheric breakdown products of tetraethyl lead, and may be longer- lived in the atmosphere. The levels of diethyl and triethyl lead compounds found appeared to account for the total amount of organolead in the samples, which was also measured. This suggests that significant quantities of tetraethyl were not present. No methyl-lead compounds were found.
Mercury	I	• Landers et al., 1995 (U.S. Arctic)
Cadmium	II	• Davidson et al., 1981(Greenland) cadmium found in wet deposition • Cheam et al., 1996 (Canadian Arctic snow) • Boutron et al., 1995, measured the trends of Cd in Greenland snow and ice cores, for the period from 1750 to the present. The concentration of Cadmium rose by a factor of about 5 between 1750 and the mid-1960's. Between the mid-1960's and the early 1990's, the concentration of Cd in the snow had decreased by a factor of about 2.5 • Ford et al., 1995, measured cadmium levels in vegetation (moss) in the U.S. Arctic. They found highly variable levels between different sites. The authors stated an opinion that long-range atmospheric transport of cadmium was not important.
Tributyltin	II	
ORGANOCHLORINE BIOCIDES		
Aldrin	I	
Dieldrin	I	• Atlas & Giam, 1981; Atlas & Schauffler, 1990 (atmosphere above the North Pacific Ocean) • Bidleman et al., 1990a (Canadian Arctic)
DDT	I	• Calamari et al, 1991 (Antarctic, etc.) • Bidleman et al., 1990a (Canadian Arctic)
DDD	I	
DDE	I	• Atlas & Giam, 1981 (atmosphere above the North Pacific Ocean) • Calamari et al., 1991 (Antarctic, etc.)
Mirex	I	
Toxaphene	I	• Bidleman et al., 1990a (Canadian Arctic)
Endrin	II	
Heptachlor	II	
Heptachlor Epoxide	II	• Welch et al., 1991 (Canadian Arctic)

Table 7. Examples of Empirical Evidence for Long Range Atmospheric Transport		
Chemical or Group	**Level (b)**	**Examples of studies which have found compound in remote areas, i.e., areas believed to be distant from any source of the particular compound**
α-**Hexachlorocyclohexane**	II	• Atlas & Giam, 1981 (atmosphere above the North Pacific Ocean) • Calamari et al., 1991 (Antarctic, etc.) • Bidleman et al., 1990a (Canadian Arctic)
β-**Hexachlorocyclohexane**	II	
δ-**Hexachlorocyclohexane**	II	
γ-**Hexachlorocyclohexane (Lindane)**	II	• Atlas & Giam, 1981 (atmosphere above the North Pacific Ocean) • Calamari et al., 1991 (Antarctic, etc.) • Bidleman et al., 1990a (Canadian Arctic)
Methoxychlor	II	• Welch et al, 1991 (Canadian Arctic)
Pentachlorophenol	II	
INDUSTRIAL / MISCELLANEOUS		
Octachlorostyrene	I	
3,3'-Dichloro-benzidene	II	
4,4'-Methylene bis (2-Chloroaniline)	II	
4-Bromophenyl Phenyl Ether	II	
Hexachloro-1,3-Butadiene	II	• Class & Ballschmiter, 1986
CHLOROBENZENES		
1,4-dichlorobenzene	II	
Tetrachlorobenzenes	II	• Atlas & Schauffler, 1990 (atmosphere above the North Pacific Ocean) (1234 & 1245 TCB measured)
Pentachlorobenzene	II	• Atlas & Schauffler, 1990 (atmosphere above the North Pacific Ocean)
Hexachlorobenzene	I	• Atlas & Giam, 1981; Atlas & Schauffler, 1990 (atmosphere above the North Pacific Ocean) • Calamari et al., 1991 (Antarctic, elsewhere) • Bidleman et al., 1990a (Canadian Arctic)
POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS (PCDD/F'S)		
PCDD/F's (as a group)	I	• Rappe et al. (1989) and Tysklind et al. (1993) compared measured atmospheric concentrations of PCDD/F at locations in Sweden to modeled back-trajectories of the air masses sampled, and found evidence that long-range atmospheric transport of these compounds was occurring. • Grundy et al. (1995) found relatively high levels of PCCD/F in soils around military installations in the Canadian arctic, and found lower, but detectable concentrations in "pristine" areas, at least 20 km away from any human activity
POLYCHLORINATED BIPHENYLS (PCB'S)		

Table 7. Examples of Empirical Evidence for Long Range Atmospheric Transport		
Chemical or Group	**Level (b)**	**Examples of studies which have found compound in remote areas, i.e., areas believed to be distant from any source of the particular compound**
PCB's (as a group)	I	• Barrie et al., 1992 • Bidleman et al., 1990a (Canadian Arctic) • Atlas & Giam, 1981; Atlas & Schauffler, 1990 (atmosphere above the North Pacific Ocean) • Bright et al. (1995) found relatively high levels of PCB's in soils around military installations in the Canadian arctic, and found lower, but detectable concentrations in "pristine" areas, at least 20 km away from any human activity; the pristine samples were enriched in lower chlorinated congeners, consistent with long-range transport considerations
POLYCYCLIC AROMATIC HYDROCARBONS		
Dinitropyrenes	II	• Gibson et al. (1986) found nitro-PAH's in remote areas (as cited in Bidleman et al., 1990b)
Benzo (a) Pyrene	I	• Daisey et al., 1981 (U.S. Arctic) • Jaffrezo et al., 1994 (Greenland snow) • Knulst et al., 1995, did find this PAH in about half of the samples of humus and moss analyzed from background sites in Sweden; in the other half, the levels were below the detection limit
Phenanthrene	II	• Daisey et al., 1981 (U.S. Arctic) • Jaffrezo et al., 1994 (Greenland snow) • Knulst et al., 1995, did find this PAH in humus and moss in background sites in Sweden
Anthracene	II	• Daisey et al., 1981 (U.S. Arctic) • Knulst et al., 1995, did not, however, find this PAH in humus and moss at background sites in Sweden
Benz (a) Anthracene	II	• Jaffrezo et al., 1994 (Greenland snow) • Knulst et al., 1995, did find this PAH in humus and moss in background sites in Sweden
Perylene	II	• Daisey et al., 1981 (U.S. Arctic) • Knulst et al., 1995, did not, however, generally find this PAH in humus and moss in background sites in Sweden; it was not detected in any of 11 humus samples, and was only detected in 1 of 11 moss samples.
Benzo (g,h,i) Perylene	II	• Daisey et al., 1981 (U.S. Arctic) • Jaffrezo et al., 1994 (Greenland snow) • Knulst et al., 1995, did find this PAH in humus and moss at most background sites in Sweden
PAH's added to ANALYZE as a GROUP(see note a)		• Daisey et al., 1981 (U.S. Arctic): fluoranthene, pyrene, chrysene, benzo(e)pyrene • Jaffrezo et al., 1994 (Greenland snow): naphthalene, fluoranthene, pyrene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene • Knulst et al., 1995, found the following PAH's in humus and moss in background sites in Sweden: Indeno(1,2,3-c,d)Pyrene, Dibenz (a,h) Anthracene; Benzo (bjk) Fluoranthenes (b+j+k combined), Fluoranthene, Benzo (e) Pyrene, Pyrene, and Chrysene • Knulst et al., 1995, did **not** find the following PAH's in humus and moss in background sites in Sweden: Naphthalene, Acenaphthene, Acenaphthylene, Fluorene

Table 7. Examples of Empirical Evidence for Long Range Atmospheric Transport		
Chemical or Group	**Level (b)**	**Examples of studies which have found compound in remote areas, i.e., areas believed to be distant from any source of the particular compound**
PAH's (as a group)	II	• Daisey et al., 1981, found PAH's in the Arctic aerosol at Barrow, Alaska and attributed their presence to long range atmospheric transport (and, for some PAH's, possibly to local sources as well) • Bidleman et al., 1990b cite several studies which have demonstrated the long range atmospheric transport of PAH's. • Welch et al., 1991, found elevated levels of high molecular weight PAH's in lake sediments in the Canadian Arctic, and concluded that the source was probably long-range atmospheric transport. • Atlas & Schauffler (1990) found only very low concentrations of PAH's in the atmosphere above the North Pacific Ocean, and cite other examples in the literature suggesting a rapid fall off in atmospheric concentration with distance from the source. Nevertheless, differences in concentrations observed could be at least partially explained by a consideration of air-mass back trajectories, with the highest concentrations of PAH's found when the air mass had traversed source regions. While organochlorine levels generally had similar values to other studies over marine sites in the Northern Hemisphere, the PAH concentrations found by Atlas & Schauffler were much lower than found in other studies. This led the authors to suggest that the atmospheric stability of PAH's is less than that of most organochlorines. • Jaffrezo et al., 1994, found PAH's in ice cores in Greenland • Knulst et al., 1995, found relatively non-volatile PAH's in humus and moss in background sites in Sweden; relatively volatile PAH's were **not** found (e.g., Naphthalene, Acenaphthene, Acenaphthylene, Fluorene, Anthracene) • Aamot et al., 1996, found the geographical pattern of 4 and 5 ring PAH's in Norwegian forest soils to be consistent with long range atmospheric transport
Abbreviations and Notes for above Table		
(a) Individual compounds added to consider PAH's as a group included: Naphthalene (Naph): Acenaphthene (Acn); Acenaphthylene (Acl); Fluorene (Flr); Indeno(1,2,3-c,d)Pyrene (IPyr); Dibenz (a,h) Anthracene (dBA); Benzo (b) Fluoranthene (BbF); Benzo (j) Fluoranthene (BjF); Benzo (k) Fluoranthene (BkF); Benzo (e) Pyrene (BeP); Pyrene (Pyr); Fluoranthene (Fln); and Chrysene (Chr)		
(b) "Level" refers to the compounds assignment in the Binational Virtual Elimination Strategy as a Level I or Level II compound; it does not refer to its capability or evidence for long-range air transport [see Table 1]		

D.   Synthesis and Summary of Information Regarding the Potential for Long Range Atmospheric Transport of Substances

For each compound or group of compounds considered in this analysis, the various atmospheric removal mechanisms discussed above will play a greater or lesser role, depending on the physical-chemical properties of the pollutant in the atmosphere. In the real world, all of the processes are happening simultaneously, and the pollutants are subjected to movement in the atmosphere due to convective and diffusive processes. For a given parcel of air containing a given pollutant, the factors governing atmospheric fate and transport will vary from moment to moment, i.e., temperature, concentration of reactive species, atmospheric aerosol, humidity, precipitation intensity, intensity of solar radiation and other factors will change continuously throughout a pollutant's atmospheric lifetime. The changing factors are frequently interrelated. For example, during a warm summer day, the temperature may favor a particular compound (e.g., 2,3,7,8-TCDD) existing more in the vapor phase, where it is more vulnerable to chemical reaction and photolytic breakdown. During the winter, the same pollutant might be more associated with particles and somewhat protected from such destruction.

Because of the complicated interrelationships, these various factors generally combine in non-linear ways. In this analysis, the various fate and transport mechanisms have been treated, more or less, in isolation, although, in a crude way, an attempt was made to include the effect of vapor/particle partitioning in the consideration of various removal mechanisms. Ultimately, a useful exercise is to combine a mathematical description of all of the fate and transport processes together, and attempt to *model* the fate of pollutants emitted to the atmosphere. To the extent that the relevant physical and chemical processes are understood and have been adequately characterized, modeling can be a useful way to develop more accurate estimates of atmospheric fate and transport. Models need to be connected, of course, to experimental, real-world data in at least two ways. First, a wide range of experimental data will generally need to be considered in the formation of the basic theoretical and/or empirical characterizations of environmental phenomena. Second, to the greatest extent possible, validation tests of the model components and of the overall model — based on real-world measurements — should be carried out.

This analysis has not included quantitative, integrated modeling in its scope, due to time limitations. Instead, a qualitative approach to the assessment of long-range atmospheric transport has been taken. In this approach, pollutants have been generally categorized as to the relative importance of various fate mechanisms.

It must be stated that for some compounds, the grasshopper effect may substantially increase the ultimate distance that the pollutant can travel in the atmosphere. Secondly, the rates of reaction with hydroxyl radical used in this screening level approach may underestimate the atmospheric lifetime for transport to remote northern regions. Thus, it is likely that for some compounds, the rough estimates made here represent a lower-bound estimate of the potential extent of atmospheric transport.

A basic question arises regarding the extent of transport that might be expected in a particular atmospheric lifetime. That is, if a compound is expected to have a lifetime of approximately 1 week, how far will it typically be able to travel in that time? Obviously, the travel length will depend on the time and location of the pollutant emission, as the meteorological parameters that influence atmospheric transport vary substantially in space and time.   One estimate of mean atmospheric transport velocities gives a value of 480 km/day for one day, and 310 km/day for five days (Summers and Young, 1987). Dennis *et al.* (1996) use an average transport velocity of 4 meters/sec (~ 350 km/day) to provide an overall estimate of the spatial scale of transport of atmospheric pollutants. Using the "average" value of 4 meters/sec, the following transport distances are estimated:

Table 8. Approximate Atmospheric Transport Distances Associated with Given Atmospheric Transport Times	
transport time	transport distance (km) assuming 4 meters/sec average atmospheric transport velocity
1 minute	0.24
10 minutes	2.4
1 hour	14
10 hours	140
1 day	350
2 days	700
1 week	2,400
2 weeks	4,800
1 month	10,500
3 months	31,000
1 year	125,000
2 years	250,000

The numbers in the above table are obviously just rough, average estimates, and the behavior at any given time and location for a particular pollutant might be much different from these values. For example, under conditions of very calm, stagnant meteorological conditions, a pollutant may stay in the same general location for days. Under very windy conditions, a pollutant might be moved much greater distances than

shown in the above table.

Based on these considerations, an attempt has been made to qualitatively estimate the atmospheric lifetimes of each of the pollutants considered in this analysis. A "Long Range Air Transport Potential" rating scale of 1-4 is defined as follows:

- Rating = 1   The pollutant is extemely long-lived in the atmosphere, with an atmospheric lifetime of on the order of a year or longer; distribution of the pollutant will be global. With the rough distance estimates above, a compound being transported at an average velocity of 4 meters per second for one year will travel on the order of 125,000 km, about three times the circumference of the earth. *Some* of the compounds in this class will likely be experience the grasshopper effect, and undergo many hops, while *some* may be so volatile that they are not significantly deposited.

- Rating = 2   The pollutant is relatively long-lived in the atmosphere, with atmospheric residence times on the order of at least a week to perhaps several months; long range transport can definitely occur over 1000's to 10,000's of kilometers. Using the above rough transport distance estimates, this class of compound could travel on the order of 2,000 - 20,000 km from the source, on average. At the high end of this range, a transport distance of 20,000 km means the distribution will be virtually global. *Some* of the compounds in this class will likely be experience the grasshopper effect, and undergo many hops, while *some* may be so volatile that they are not significantly deposited.

- Rating = 3   The pollutant is relatively short-lived in the atmosphere, with atmospheric residence times on the order of several hours to a few days; atmospheric transport may occur on regional, mesoscale distances. Using the above rough transport distance estimates, this class of compound could travel on the order of 30 - 1000 km from the source, on average. Since the atmospheric lifetime for these compounds may be shorter than the characteristic time of a grasshopper effect "hop", many of these compounds may not exhibit this phenomenon — i.e., they may not survive long enough (on average) in the atmosphere to make it through even their "first" hop.

- Rating = 4   The pollutant is extremely short-lived in the atmosphere, with atmospheric residence times on the order of seconds to minutes to at most an hour or so; with such pollutants, atmospheric transport of emissions will be limited to the local region around the source. Using the above rough transport distances, one could say that compounds in this class would be limited, on average, to transport within a local area within 0.1 - 10 km from the source. Certainly for

these compounds, it is unlikely that any will survive long enough (on average) in the atmosphere to make it through even one hop and so, it is unlikely that any of them will participate in the grasshopper effect.

This qualitative categorization and rating scheme is summarized in Table 9.

In Table 10, the information relevant to the Long Range Air Transport Potential is summarized for each compound or group of compounds considered, and an estimate of the overall rating is made for each.

L.R.T. Rating	Phase	Volatility	Reactivity and/or Photolytic Degrad-ability	Henry's Law Rainout Potential	Particle Size	Atmospheric Fate	Approximate Atmospheric Lifetime	Examples
Table 9. Types of Atmospheric Pollutants, With Particular Attention to the Properties that Influence Long Range Transport and Potential Deposition								
1	vapor	very volatile	minimally reactive	minimally soluble		may not be deposited significantly from the atmosphere to the Great Lakes because compound is relatively volatile	~ months to years	Hexachloro-1,3-butadiene
4			very reactive			atmospheric lifetime on the order of seconds, minutes, or hours; thus, unlikely to be transported long distances	~ minutes to hours	Aldrin
3				very soluble		vulnerable to rain washout, but since rain is sporadic, will probably have lifetime on the order of a week — capable of being transported moderately long distances	~ 1-2 weeks	3,3'-Dichloro-benzidene
1		semi-volatile	minimally reactive	minimally soluble		capable of being transported extremely long distances in the atmosphere; may undergo the grass-hopper effect.	~ 1 year or longer	Hexachloro-benzene
2	vapor/ particle: exchange-able	semi-volatile	minimally reactive		full range	capable of being transported long distances in the atmosphere; grass-hopper effect will likely extend transport distances considerably.	~ weeks to months	PCB's (esp. with, e.g., 4-8 chlorines)
3			moderately reactive		full range	may be somewhat protected from reaction and photolytic degradation when on particles; when in vapor phase, more vulnerable; capable of being transported moderately long distances; grass-hopper effect may extend transport distances, but compounds may undergo substantial degradation during each hop.	~ days	2,3,7,8-TCDD
4	particle				large	large particle lifetimes relatively short; thus potential for long range atmospheric transport is generally low	~ minutes to hours	pollutants associated with *portions* of windblown dust
2					small	small particle lifetimes are moderately long, on the order of 1-2 weeks; thus, there is a potential for long range atmospheric transport	~ 1-2 weeks	Cadmium emissions from incineration
3-4			reactive			particle phase reactions degrade compounds relatively quickly; reduced potential for long range transport, even on small particles	~ hours to days	PAH's on wood smoke particles

Table 10. Overall Summary of Compounds Considered in this Evaluation
(See Notes Following Table for Column Descriptions, Codes Used, and Other Information)

Chemical or Group	Level	Is the Atmosphere a Potentially Important Transport Pathway?		Long Range Atmospheric Transport Potential						L.R.T. Evidence	Overall L.R.T. Rating
		Emitted to the Air?	Measured / Found in Atm?	Phase in Atm	Resistant to Gas Rxn?	Photolytic Resistance	Gas Washout Resistance?	Small Particles in Atm?	Avg Atm Lifetime	Measured / Found in Remote Areas?	LRT Potential (Rating)
COLUMN # --> (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
METALS / ORGANOMETALLICS											
Alkylated Lead	I	1	1	(V V)	(½)	?	(½)	(1)	(1 wk)	1	2
Mercury	I	1	1	v	1	1	¾ (?)	(1)	(1 yr)	1	1
Cadmium	II	1	1	P P	1	1	1 (?)	1	(1 wk)	1	2
Tributyltin	II	?	?	v/p	0	1	1	~ 1 (?)	?	?	(3 ?)
ORGANOCHLORINE BIOCIDES											
Aldrin	I	1	1	V V	0	(½)	1	-	<1 day	?	3 - 4
Dieldrin	I	1	1	V V	¼	(½)	1	-	1 day	1	3
DDT	I	1	1	v/p	½	1	1	1	(1 wk)	1	2
DDD	I	1	1	v/p	½	(½)	1	1	(1 wk)	?	2
DDE	I	1	1	v/p	¼	½	1	1	(1 wk)	1	2
Mirex	I	1	½	(V V)	1	1	1	-	>1wk?	?	2
Toxaphene	I	1	1	v/p	½	1	1	½ - 1	1 wk	1	2
Endrin	II	1	1	V V	0	½	1	-	1 day	?	3
Heptachlor	II	1	1	V V	0	½	1	-	<1 day	?	3 - 4
Heptachlor Epoxide	II			V V	½	1	1	-	3 days	1	3
α-Hexachlorocyclohexane	II	1	1	V V	1	(¾ -1)	(½-¾)	-	1 mo?	1	2
β-Hexachlorocyclohexane	II	1	1	V V	1	¾ -1	(½-¾)	-	1 mo?	?	2
δ-Hexachlorocyclohexane	II	1	1	V V	1	(¾ -1)	(½-¾)	-	1 mo?	?	2
(Lindane) γ-Hexachlorocyclohexane	II	1	1	v	1	1	(½-¾)	(1)	1 mo?	1	2
Methoxychlor	II	1	1	v/p	¼	1	1	(1)	2 days	1	3
Pentachlorophenol	II	1	1	V V	1	¼	¾ -1	-	1 wk	?	2
INDUSTRIAL / MISCELLANEOUS											
Octachlorostyrene	I	1	1	v	¾	(1) ?	1	(1)	>1wk?	?	2
3,3'-Dichlorobenzidene	II	½	?	v/p	½	¼ - ½	½	(1) (?)	1 wk	?	2
4,4'-Methylene bis (2-Chloroaniline)	II	1	1	v	0	?	0	(1) (?)	<1 day	?	3 - 4
4-Bromophenyl Phenyl Ether	II	~ 1	?	V V	¼	?	1	-	2 days	?	3
Hexachloro-1,3-Butadiene	II	1	1	V V	1	(1)	1	-	1 yr	1	1

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Table 10. Overall Summary of Compounds Considered in this Evaluation
(See Notes Following Table for Column Descriptions, Codes Used, and Other Information)

| Chemical or Group | Level | Is the Atmosphere a Potentially Important Transport Pathway? | | Long Range Atmospheric Transport Potential | | | | | | L.R.T. Evidence | Overall L.R.T. Rating |
| | | | | Assessment of Factors Influencing Fate and Transport in the Atmosphere | | | | | | | |
		Emitted to the Air?	Measured / Found in Atm?	Phase in Atm	Resistant to Gas Rxn?	Photolytic Resistance	Gas Washout Resistance?	Small Particles in Atm?	Avg Atm Lifetime	Measured / Found in Remote Areas?	LRT Potential (Rating)
COLUMN # --> (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
CHLOROBENZENES											
1,4-dichlorobenzene	II	1	1	V V	1	1	1	-	1 mo	?	2
Tetrachlorobenzenes	II	1	1	V V	1	1	1	-	4 mo	1	1
Pentachlorobenzene	II	1	1	V V	1	1	1	-	6 mo	1	1
Hexachlorobenzene	I	1	1	V V	1	1	1	-	2 yrs	1	1
POLYCHLORINATED DIBENZO-*p*-DIOXINS & DIBENZOFURANS (PCDD/F'S)											
PCDD/F's	I	1	1	v/p	1	½	1	1	(1 wk)	(½)	2
POLYCHLORINATED BIPHENYLS (PCB'S)											
PCB's	I	1	1	v/p	½ - 1	¾ -1	1	½	(1 wk)	1	2
POLYCYCLIC AROMATIC HYDROCARBONS											
Dinitropyrenes	II	1	1	v/p	?	½	1	(1)	(1 wk)	(1)	2
Benzo [a] Pyrene	I	1	1	p	½	½	1	(1)	(1 wk)	(1)	2
Phenanthrene	II	1	1	(V V)	¼	¼	½	(1)	(1day)	1	3
Anthracene	II	1	1	V V	0	0 - ¼	½	(1)	(1day)	½	3
Benz [a] Anthracene	II	1	1	v/p	¼	½	½	(1)	(1 wk)	1	2
Perylene	II	1	1	p	½	(½)	1	(1)	(1 wk)	(½)	2
Benzo [g,h,i] Perylene	II	1	1	p	½	(¾)	1	(1)	(1 wk)	1	2
PAH's (as a group)	II	1	1	v/p	0 - 1	½	1	(1)	(1 wk)	(½ - 1)	2

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Codes and Notes for Table 10

A. Some General Features of the Table, common to some or all columns

- In columns 3 through 9, and column 11, as described in detail below, an entry of "1" indicates that, all things being equal, the compound or group is expected to be capable of being transported for long distances in the atmosphere; in other words, *this particular factor does not appear to rule out long range atmospheric transport.*

- In these same columns, as described below, an entry of "0" indicates that the particular factor significantly limits the atmospheric lifetime of the compound in the atmosphere, making long range atmospheric transport unlikely. *Thus, if there is a "0" in any of the columns 3 - 9 or 11, then this suggests that long range atmospheric transport is not expected to be significant for the compound or compound group.*

- Again, in these same columns, as described below, an entry of "¼" or "½" or "¾" suggests that the particular factor has an intermediate significance, placed between the two extremes of "1" and "0"

- a dash, "-", indicates that the factor is not applicable.

- an entry in parentheses -- e.g., "(1)" -- indicates that an educated guess is being made and that the estimate is *relatively* uncertain.

- a question mark — "?" — as an entry means that the piece of information might be relevant, but, no information could be found. If an estimate is provided, it is *very* uncertain

B. Descriptions of Columns in Table 1

(1) Chemical or Group:

Many of the "chemicals" on this list are really groups of chemicals. In these cases, an overall evaluation of the group was attempted.

(2) Level:

Level I Substances are the 11 Critical Pollutants identified by the IJC's Great Lakes Water Quality Board, plus one additional Critical Pollutant identified by the Lake Superior LaMP and the Lake Ontario Toxics Management Plan (Octachlorostyrene). Note: Chlordane was also an additional Critical Pollutant identified, but it was not included on the target list for this analysis.

Level II Substances are those substances identified by the Canada-Ontario Agreement respecting the Great Lakes Basin Ecosystem (COA) as "Tier II" chemicals, plus additional substances of concern identified by LaMP and RAP processes and the Great Lakes Water Quality Guidance in the U.S.

(3) Emitted to the Air?:

0   =   Pollutant is not considered be emitted to the air in potentially significant quantities.

1   =   Pollutant is considered to be emitted to the air in potentially significant quantities.

(4)   Measured / Found in Atm?:

1   =   Attempt(s) have been made to measure the compound in the atmosphere, and it has been found in at least some of the measurements

0   =   Attempt(s) have been made to measure the compound in the atmosphere, and it is never or rarely found

(5)   Phase in Atm:

P P   =   Compound is expected to exist almost entirely in the particle phase in the atmosphere (fraction adsorbed $\geq$ 98% under all conditions)

p   =   Compound is expected to exist mostly in the particle phase in the atmosphere (fraction adsorbed $\geq$ 90% under all conditions)

v/p   =   Compound is expected to exist in significant proportions in both the particle phase and the vapor phase as conditions vary

v   =   Compound is expected to exist mostly in the vapor phase in the atmosphere (fraction adsorbed $\leq$ 10% under all conditions)

V V   =   Compound is expected to exist almost entirely in the vapor phase in the atmosphere (fraction adsorbed $\leq$ 2% under all conditions)

(6)   Resistant to Gas Rxn?:

1   =   Compound is predicted to be relatively resistant to gas-phase reaction in the atmosphere with hydroxyl radical (in some cases, reaction with ozone was also considered), either because it exists largely in the particle phase, or, because its predicted reaction rate with hydroxyl radical is relatively low

0   =   Compound is predicted to be very susceptible to gas-phase reaction in the atmosphere with hydroxyl radical (in some cases, reaction with ozone was also considered), because the compound exists to a significant extent in the gas phase, and, because its reaction with hydroxyl radical (or, in some cases, ozone) is relatively rapid

(7)   Photolytic Resistance?:

1   =   Compound is predicted to be relatively resistant to photolysis by ultraviolet light in the atmosphere, either because it does not appear to have significant absorption peaks at uv wavelengths greater than 290 nm, or, because it exists largely in the particle phase.

0   =   Compound is predicted to be very susceptible to photolysis by ultraviolet light in the atmosphere, because it exists in the gas phase, and, it either appears to have very strong absorption peaks at uv wavelengths greater than 290 nm, or, other strong evidence for atmospheric photolysis exists.

(8)   Gas Washout Resistance?:

1   =   Compound is predicted to be relatively resistant to gas phase wet deposition by precipitation, either because it does not exist to a great extent in the vapor phase, or, because its Henry's Law constant (atm-m3/mol) is relatively large (i.e., the compound is not particularly water soluble and, when given a choice between the water and vapor phase in the atmosphere, does not significantly partition to the aqueous phase).

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0   =   Compound is predicted to be relatively vulnerable to gas phase wet deposition by precipitation, because it exists to a great extent in the vapor phase, and, because its Henry's Law constant (atm-m3/mol) is relatively small (i.e., the compound is relatively water soluble and, when given a choice between the water and vapor phase in the atmosphere, it will partition significantly to the aqueous phase).

(9)   Small Particles in Atm?:

1   =   When or if the compound is associated with particles in the atmosphere, a substantial fraction is associated with small particles, generally less than about 1 - 2 µm in diameter.

0   =   The bulk of the compound in the atmosphere is associated with large particles -- i.e., greater than about 5 - 10 µm in diameter. Such particles have a relatively short atmospheric lifetime and thus, the potential for long range atmospheric transport would be limited.

½   =   Significant fractions have been found (or are estimated) to exist in fine *and* coarse particles, or, with particles of intermediate size (i.e., on the order of 2 - 5 µm in diameter).

(10)   <u>Avg Atm Lifetime (days, unless otherwise noted)</u>

Based on the preceding columns, information contained in this analysis, or information from the literature, a very rough estimate of the mean atmospheric lifetime of the pollutant is given. There are many uncertainties in these estimates, and these are regarded — at best — as only very rough order-of-magnitude estimates. Various limitations of these estimates are discussed throughout the text. *Note that some of the more volatile or mid-range volatile compounds probably are involved in the grasshopper effect. For these compounds with atmospheric lifetimes of ~ 1 week (or longer), they probably survive long enough in the atmosphere to experience multiple hops. For such compounds with very long lifetimes, e.g, hexachlorobenzene, they probably experience many, many such hops, with very little degradation while airborne during each hop.*

(11)   <u>Measured / Found in Remote Areas?</u>

1   =   Attempt(s) have been made to measure the compound in remote areas — far from any sources -- in the atmosphere, atmospheric deposition (e.g., precipitation), vegetation, or other environmental media with relatively direct links to atmospheric pollutants.

0   =   Attempt(s) have been made to measure the compound in remote areas, as described above, and it is never or rarely found

(12)   L.R.T. (Long Range Transport) Potential (Rating)

(see text in section D).

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